Charge Transfer Based Colorimetric Detection of Silver Ion

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Received November 6, 2013, Accepted January 13, 2014

Key Words: Charge-transfer interaction, Chemosensor, Colorimetry, Silver ion

Donor–acceptor interactions or charge transfer (CT) interactions1 are an important class of non-covalent interactions and have been widely exploited in self-assembling systems. Beyond molecular chemistry, supramolecular chemistry aims at constituting highly complex, functional chemical systems from components held together by intermolecular forces. Chemosensors are the molecules of abiotic origin that bind selectively and reversibly with the analyte with concomitant change in one or more properties of the system. The recognition and signaling of ionic and neutral species of varying complexity is one of the most intensively studied areas of contemporary supramolecular chemistry.2 Among different types of chemosensors, colorimetric/chromogenic chemosensors are especially attractive because the guest determination can be carried out by the naked eye, without the use of expensive equipment and they also find direct applications in the development of optodes and disposable dip-stick arrays based on absorption changes.3 Although molecules containing an electron donor and an electron acceptor linked by a spacer have also been studied extensively in conjunction with the development of stable intra-molecular CT complex,4,5 to the best of our knowledge, there is no report to sense the analyte using molecules containing an electron donor and an electron acceptor linked by a spacer. In continuation with our research on the self-assembling supramolecular systems via donor–acceptor interactions,6 we were intrigued to apply this interaction for signaling of ionic species. Herein we report on the design and synthesis of U-shape molecule which is linked by oligoethylene glycols (OEGs) between an electron-deficient (methyl viologen; MV₂⁺) and an electron-rich (2,6-diakloxy-naphthalene; Np) units and their application on sensing metal ion (Figure 1).

Experimental Section

Compound 4. A mixture of 6-methoxy-2-naphthol (128 mg, 0.73 mmol) and compound 3 (500 mg, 0.73 mmol) in acetone (30 mL) in the presence of potassium carbonate (203 mg, 1.46 mmol) was refluxed for 14 h. The resulting mixture was diluted with EtOAc and filtered and the filtrate was concentrated and purified by column chromatography (EtOAc/hexane system) to afford the pure product 4 (215 mg, 40%). This reaction also afforded byproduct which is compound 5. 1H-NMR (300 MHz, CDCl₃) δ 3.21 (t, J = 6.9 Hz, 2H), 3.62-3.72 (m, 18H), 3.81-3.90 (m, 9H), 4.13-4.14 (m, 4H), 4.18 (t, J = 7.8 Hz, 2H), 6.88 (m, 4H), 7.07-7.16 (m, 4H), 7.59 (d, J = 3.9 Hz, 1H), 7.62 (d, J = 4.0 Hz, 1H); 13C-NMR (75 MHz, CDCl₃) δ 2.9, 55.1, 67.3, 68.6, 69.5, 70.0, 70.36, 70.45, 70.49, 70.6, 71.7, 105.8, 106.9, 114.7, 118.7, 119.0, 121.4, 127.9, 128.0, 129.4, 129.6, 148.7, 155.0, 155.9; MS (FAB): m/z 728.46 [M⁺]; HRMS (FAB): Calcd for C₃₃H₄₅IO₁₀: 728.2057. Found: 728.2072 [M⁺], 729.2130 [M⁺+H].

Compound 1. A solution of N-methyl-4,4'-bipyridinium iodide (18.3 mg, 0.06 mmol) and compound 4 (53.7 mg,
0.07 mmol) in DMF (0.12 mL) was stirred for 2 days at 80 °C and then cooled to room temperature. Then THF was added to precipitate the product. The precipitates were collected by the filter or centrifugation and washed with THF. The solids were dried in vacuum to afford the desired product 1 (61 mg, 95%). 1H-NMR (500 MHz, D2O) δ 3.70-3.74 (m, 8H), 3.76-3.82 (m, 12H), 3.88 (s, 3H), 3.90-3.92 (m, 4H), 3.95 (t, J = 4.0 Hz, 2H), 4.09 (t, J = 4.5 Hz, 2H), 4.13 (br, 2H), 4.37 (s, 3H), 4.84 (t, J = 4.5 Hz, 2H), 6.68-6.79 (m, 4H), 6.93 (dd, J1 = 9.0 Hz, J2 = 2.5 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 7.04 (dd, J1 = 9.0 Hz, J2 = 2.5 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 7.49 (d, J = 2.0 Hz, 1H), 7.50 (d, J = 2.5 Hz, 1H), 8.03 (d, J = 7.0 Hz, 2H), 8.13 (d, J = 7.0 Hz, 2H), 8.73 (d, J = 6.5 Hz, 2H), 8.96 (d, J = 6.5 Hz, 2H); 13C-NMR (75 MHz, D2O) δ 49.2, 55.1, 61.9, 67.2, 68.7, 69.1, 69.5, 70.1, 70.2, 70.4, 70.5, 70.6, 105.4, 106.6, 114.3, 118.3, 118.7, 122.5, 127.1, 127.2, 127.5, 127.6, 129.1, 129.3, 146.4, 146.7, 149.6, 150.3, 154.7, 155.6; MS (FAB): m/z 899.03 [M+-I], 772.21 [M+-2I]; HRMS (FAB): C44H56I2N2O10: 1026.2024. Found: 899.2977 [M+-I].

Results and Discussion

An early landmark in the development of receptors for group I metal cations was Pedersen’s observations of the formation of side products during the synthesis of ‘metal deactivators’ for use in the stabilization of rubber.7 The ensuing decade brought further notable advances through the use of the principles of shape and size complementarity which is important key in the design and construction of chemosensors for cations.8 In this sensing process, information at the molecular level, such as the presence or not of a certain guest in solution, is amplified to a macroscopic level so that sensing might open the door to qualitative or quantitative determination of certain guests.

The synthesis of U-shape molecule, linked by oligoethylenglycols between an electron-deficient (methyl viologen; MV2+) and an electron-rich (2,6-dialkoxy naphthalene; Np) units, is shown in Scheme 1. Bis-O-alkylation of catechol with iodo-tetraethylene glycol afforded compound 2 in 64% yield. Diiodo compound 3 was obtained in yield of 94% by mesylations of diols 2 with MsCl and followed by iodinations with sodium iodide. Nucleophilic displacement of one iodo group in 3 with 6-methoxy-2-naphthol gave compound 4 in 40% yield. Finally, reaction of 4 with 1-methyl-4-(4-pyridyl)-pyridinium iodide provided the desired compound 1 in yield of 95%. The chemical structures of these compounds were confirmed by 1H- and 13C-NMR spectroscopy, IR spectroscopy, and mass spectrometry.

First of all, we examined the host induced intramolecular CT complex. Treatment of 1 equiv of CB[8] into a solution of compound 1 resulted in a drastic change in the UV/Vis

Scheme 1. Synthesis of compound 1.
The high selectivity obtained in sensing metal ions by various metal ions evaluated by the color change is photochemically presented in Figure 3. Furthermore, various metal ions evaluated by the color change is photochemically presented in Figure 3. The appearance of new absorption bands at $\lambda = 544$ nm supports the formation of the charge transfer complex 1* between an electron-deficient (methyl viologen; MV$^{2+}$) and an electron-rich (2,6-dialkoxynaphthalene; Np) units inside the hydrophobic cavity of CB[8]. And then we tried to sense metal ions using CT complex 1*. Figure 2 shows the absorption spectra of 1* ($5.0 \times 10^{-4}$ M in H$_2$O) and those in the presence of various metal ions. No significant change in the absorption of CT complex 1* was observed upon the addition of various metal ions including Na$^+$, K$^+$, Cs$^+$, Pb$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Hg$^{2+}$ (10 equiv). However, the charge-transfer complex 1* shows drastic increase of absorption intensity around 540 nm in the presence of Ag$^+$ (10 equiv). Consequently, the yellowish color of compound 1 changed to a reddish brown color upon the addition of Ag$^+$ in water and viologen units interaction.

The absorption titration spectra of compound 1 (5.0 $\times$ 10$^{-4}$ M) upon the addition of Ag$^+$ in H$_2$O are shown in Figure 4. As shown, the $^1$H-NMR titrations were carried out in CD$_2$CN to understand further structural characteristics of Ag$^+$ complexes in solution. Upon stepwise addition of Ag$^+$, the $^1$H signals for OEGs protons present at 3.6-4.0 ppm in the compound 1 were observed further broad result by the coordination of Ag$^+$ with ether oxygen atoms in the OEGs. And also, the $^1$H signals for the Np protons and the viologen protons of compound 1 shift downfield relative to those in the free compound 1 (Figure S1: see supporting information). For the viologen protons, the order of magnitude of the chemical shift variation is Hb ($\Delta$ $\delta$: 0.16 ppm) > Hd (0.15 ppm) > Hc (0.12 ppm) > Ha (0.06 ppm). The chemical shift variation seems to be caused by magnetic anisotropy effect of the Np and viologen units interaction.

Figure 2. UV-vis spectra of CT complex 1* upon the addition of various metal ions ($5.0 \times 10^{-4}$ M in H$_2$O). (a) none, (b) Na$^+$, (c) K$^+$, (d) Cs$^+$, (e) Pb$^{2+}$, (f) Zn$^{2+}$, (g) Cu$^{2+}$, (h) Ni$^{2+}$, (i) Hg$^{2+}$, and (j) Ag$^+$ (10 equiv) were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.

Figure 3. UV-vis spectra of compound 1 upon the addition of various metal ions ($5.0 \times 10^{-4}$ M in H$_2$O). (a) none, (b) Na$^+$, (c) K$^+$, (d) Cs$^+$, (e) Pb$^{2+}$, (f) Zn$^{2+}$, (g) Cu$^{2+}$, (h) Ni$^{2+}$, (i) Hg$^{2+}$, and (j) Ag$^+$ (10 equiv) were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.

Figure 4. UV-vis spectra of compound 1 upon the addition of Ag$^+$ ($5.0 \times 10^{-4}$ M in H$_2$O). (a) none, (b) 1eq, (c) 2eq, (d) 5eq, (e) 10eq, (f) 20eq, (g) 50eq, (h) 100eq, and (i) 150eq were added to each sensor solution. Photograph shows the appearance of the solutions which were allowed to stand for 6 h.
in Figure 4, the addition of Ag⁺ (1-2 equiv) had no obvious effect on the absorption band. In the case of 1-2 equiv of Ag⁺, iodide anions (2 equiv) of the viologen unit in a solution of compound 1 lead to the formation of AgI. Thus, the addition of Ag⁺ (1-2 equiv) had no dramatic color change to a reddish brown color. However, when 5-50 equiv of Ag⁺ were added to the solution of 1, dramatic color change was observed, suggesting that compound 1 might show specific response with Ag⁺ due to the chelation enhanced intramolecular CT interaction from Np to viologen moiety of compound 1. And another important reason for the color change to a reddish brown color, because it predicts that Ag nanoparticles are formed. Previous study (Li et al.) have shown that the Ag nanoparticles contribute to the absorption bands at 450-550 nm in the UV-Vis spectra. The absorption titration study shows that the absorption intensity increases as the concentration of AgNO₃ increases, which reflects in the formation of more 1-Ag⁺ complexes and Ag nanoparticles. While in the case of Ag⁺ with 100-150 equiv, color change for sensing of Ag⁺ was observed and the appearance of new absorption bands around 540 nm supports formations of 1-Ag⁺ and Ag nanoparticles. However, at a high concentration of AgNO₃ (100-150 equiv), the solutions which were allowed to stand for 6 h returned to yellowish color and had no absorption band above 500 nm. It is further noted that increasing the concentration of AgNO₃ gradually during the preparation of charge-transfer complexes led to the formation of nanoparticles and then the particles’ size was increased and precipitated over time. Oligoethylene glycols (OEGs) is also a good stabilizer for Ag nanoparticles based on the conclusions made by several research studies. In one of these research works, Luo et al. reduced AgNO₃ in the presence of OEGs. In this process, Ag⁺ was successfully reduced to Ag⁰ to form Ag nanoparticles. This shows that the reduction of the silver ions to silver atoms was continued and resulted in an increase in the concentration of Ag nanoparticles. In order to study possible mechanism of the formation of Ag nanoparticles, the compound 2, 5, and 6 in water with Ag⁺ (1-150 equiv) were conducted to examine the color change. When 1-150 equiv of Ag⁺ were added to the solutions of compound 2, 5, and 6, dramatic color change and formation of nanoparticles were not observed. Therefore, in order to the formation of Ag nanoparticles are required for CT interaction between an electron-deficient and an electron-rich units in the presence of OEGs.

In summary, we have demonstrated the colorimetric chemosensor for detection of Ag⁺ via formation of nanoparticles which is based on the intramolecular CT interaction between the electron-rich (2,6-dialkoxynaphthalene; Np) moiety and the electron-deficient (methyl viologen; MV²⁻) moiety of a single sensor molecule. Under irradiation of light, Ag⁺ was reduced to very small silver nanoparticle by CT interaction in the presence of OEGs as flexible recognition moiety of Ag⁺ and stabilizer for Ag nanoparticles, thus Ag nanoparticles resulted to reddish brown in the color change of sensor solution, gradually. Therefore, the charge-transfer interaction between an electron-deficient and an electron-rich units existing at a sensor molecule can be regarded as a new and efficient method to construct various colorimetric chemosensors.

Acknowledgments. This research was supported by the Dong-A University Research Fund.

Supporting Information. General methods, characterization data of compounds 2, 3, 5, and 6, CT complex 1*, and Figure S1.

References and Notes